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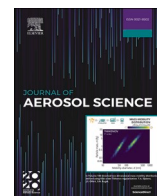
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Investigating the effectiveness of condensation sink based on heterogeneous nucleation theory

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ABSTRACT

New Particle Formation (NPF) is regularly observed to occur in heavily polluted Chinese megacities. However, in these NPF events, the survival probability of small clusters into larger aerosol particles is higher than theoretically predicted. One explanation for this could be that the loss rate of clusters due to scavenging by pre-existing particles, which is described by condensation sink, is lower than expected. In this study, we describe the loss of clusters due to condensation sink by using heterogeneous nucleation theory, and investigate if ineffectiveness of heterogeneous nucleation can result in a significantly lowered effective condensation sink. We find that in principle it is possible that due to properties of the system there is no heterogeneous nucleation, and this can significantly influence the magnitude of effective condensation sink and thus increase the survival probability of clusters.

1. Introduction

New Particle Formation (NPF) is a regularly observed atmospheric phenomenon (Kerminen et al., 2018). New particles form by clustering of vapour molecules, which is followed by their growth to larger sizes (Kulmala et al., 2014). NPF is a major contributor to aerosol particle number concentrations (Spracklen et al., 2006), and it also significantly contributes to global CCN (cloud condensation nuclei) concentrations (Merikanto et al., 2009; Spracklen et al., 2008). Aside from climate effects, aerosol particles have adverse effects on human health (Kim et al., 2015; Lelieveld et al., 2015), especially in highly urbanized regions, such as Chinese megacities (Chen et al., 2012).

NPF events are regularly observed in China in environments with high concentrations of pre-existing particles (Chu et al., 2019; Wang et al., 2013). NPF in Chinese megacities is characterised by a higher frequency and higher particle formation rates compared to more rural areas (Chu et al., 2019; Xiao et al., 2015; Yu et al., 2016). High particle formation rates have been suggested to be caused by nucleation of sulphuric acid and amines (Yao et al., 2018). In Beijing, episodes of high particulate pollution level have been observed to follow NPF events (Guo et al., 2014; Zhang et al., 2015). On the other hand, high surface area of pre-existing particles has been observed to suppress NPF in Chinese megacities (Cai et al., 2017b; Xiao et al., 2015).

To be able to detect a NPF event, a significant fraction of nanometer-sized clusters need to be able to grow to larger aerosol particles. The fraction of clusters surviving to larger particles, i.e. their survival probability, is determined by the competition between

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their growth and scavenging by pre-existing particle population (Kerminen et al., 2001; Kuang et al., 2010). Theoretically, the survival probability can be described by using Kerminen-Kulmala equation, according to which the survival probability depends on the ratio between the growth rate (GR) of particles and the loss rate due to scavenging, described by condensation sink (CS) (Kerminen & Kulmala, 2002; Korhonen et al., 2014). Recently, Kulmala et al. (2017) showed that in Chinese megacities, the theoretical survival probability of particles from 1.5 nm to 3 nm sizes should be practically zero, due to high CS. Therefore, to explain the observed NPF events in China, GR needs to be higher than currently observed, or effective CS needs to be lower than CS calculated based on the collision rates of clusters with pre-existing particles. The latter is possible if clusters are scavenged only by a small fraction of particle population.

The objective of this study is to explore the possible explanations for NPF occurring in highly polluted environments, where survival probability of particles should theoretically be negligible. More specifically, we describe the loss of clusters due to CS by using heterogeneous nucleation theory, and investigate the requirements for heterogeneous nucleation to be ineffective. Then, we use particle size distributions measured in Beijing to evaluate, how ineffectiveness of heterogeneous nucleation can result in lowered effective CS in a Chinese megacity, and thus lead to an increased survival probability of growing clusters.

2. Methods

2.1. Theoretical approach

Atmospheric NPF occurs when molecular clusters are formed by nucleation and then grow to larger sizes. The survival probability of growing clusters to larger particles is determined by the competition between their growth and coagulation scavenging according to Kerminen-Kulmala equation (Kerminen & Kulmala, 2002)

$$J_{d_2} / J_{d_1} = \exp \left[\kappa \left(\frac{1}{d_2} - \frac{1}{d_1} \right) \frac{CS}{GR} \right] \quad (1)$$

Here J_{d_1} is the formation rate of clusters with diameter d_1 and J_{d_2} is particle formation rate at a larger diameter d_2 . Parameter κ is equal to $0.23 \text{ nm}^2 \text{ m}^2 \text{ h}^{-1}$. GR is the growth rate of particles between d_1 to d_2 , which is assumed to be constant. CS is condensation sink, describing the loss rate of vapour molecules due to their collisions with pre-existing aerosol particles. CS is calculated from particle size distribution data according to (Pirjola et al., 1999)

$$CS = 2\pi D \sum_i \varepsilon_i d_i N_i, \quad (2)$$

where D is the diffusion coefficient of the vapour, d_i is diameter of particle i , ε_i is the transitional correction factor and N_i the number concentration of particle i . Diffusion coefficient is calculated based on the properties of sulphuric acid. Transitional correction factor is calculated as (Kulmala et al., 2001b)

$$\varepsilon_i = \frac{1 + Kn}{1 + 0.377Kn + \frac{4}{3}\alpha^{-1}Kn + \frac{4}{3}\alpha^{-1}Kn^2} \quad (3)$$

where α is the accommodation coefficient for mass transfer, which is assumed to be unity in our calculations. Kn is Knudsen number, $Kn = 2\lambda/d_i$, where

$$\lambda = 3 \sqrt{\frac{\pi m}{8k_b T}}, \quad (4)$$

where m is the mass of a vapour molecule, T is temperature and k_b is the Boltzmann constant.

In Chinese megacities, the observed survival probability of clusters has been found to be clearly higher than the theoretical value calculated based on Eq. (1) when GR is obtained from measurements and CS is calculated based on Eq. (2) (Kulmala et al., 2017). There can be several reasons for this, such as measurement uncertainties, underestimation of measured particle growth rate and overestimation of CS. In this study, we focus on the last option. We define effective condensation sink as

$$CS_{\text{eff}} = 2\pi D \sum_i \varepsilon_i \zeta_i d_i N_i, \quad (5)$$

where parameter ζ_i is equal to one or zero and tells whether particle with diameter d_i acts as a sink for vapour molecule or not. In this study, we calculate CS_{eff} assuming that there exist diameters for which $\zeta_i = 0$. Ratio CS_{eff}/CS can be lower than one if the clusters are not efficiently scavenged by pre-existing particles (i.e. for some particles $\zeta_i = 0$), for example due to the chemical composition of clusters and pre-existing particles. This is analogous to the case where particles composed of hydrophobic organic compounds do not activate to cloud condensation nuclei (Tandon et al., 2019).

In this study, our main assumption is that coagulation scavenging of clusters by pre-existing particles can be described by using classical heterogeneous nucleation theory, and thus ineffective heterogeneous nucleation can result in $\zeta_i = 0$ for some particle sizes. This can lead to CS_{eff} being significantly lower than CS, which increases the survival probability of clusters when CS in Eq. (1) is replaced with CS_{eff} . Our methods are described in more detail in the following sections (2.2-2.3). One should note that in our approach

we do not need to make an assumption on the nucleation mechanism, but we only assume that there is a flux of clusters, which can be formed by any mechanism.

2.2. Heterogeneous nucleation model

We calculated heterogeneous nucleation probabilities using classical nucleation theory. The free energy needed to form a critical cluster for heterogeneous nucleation (ΔG_{het}^*) can be calculated from the homogeneous free energy of formation of critical cluster (ΔG_{hom}^*) with (Fletcher, 1958)

$$\Delta G_{\text{het}}^* = f_g \Delta G_{\text{hom}}^*, \quad (6)$$

where f_g is a geometric factor. It is defined as

$$f_g = \frac{1}{2} \left[1 + \left(\frac{1 - Xm}{g} \right)^3 + X^3 \left(2 - 3 \frac{(X - m)}{g} + \left(\frac{X - m}{g} \right)^3 \right) + 3X^2 m \left(\frac{X - m}{g} - 1 \right) \right], \quad (7)$$

where

$$g = \sqrt{1 + X^2 - 2Xm}, \quad (8)$$

X is the ratio between the radius of the seed particle, R_{seed} , and the critical radius, r^* ,

$$X = R_{\text{seed}} / r^*, \quad (9)$$

and m is called the contact parameter,

$$m = \cos \theta, \quad (10)$$

where θ is a contact angle. Contact angle depends on chemical properties of the vapour and the nucleating surface, such as a seed particle. It can be described by the classical form of Young's equation (Gaydos and Neumann, 1987)

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}, \quad (11)$$

where σ_{sv} is the surface tension of solid-vapour interface, σ_{sl} is the surface tension of solid-liquid interface and σ_{lv} is the surface tension of the liquid-vapour surface tension. The contact angle upon nucleation on a spherical seed particle is illustrated in Fig. 1.

Nucleation probability in heterogeneous nucleation depends on nucleation rate, which can be expressed in a one-component case as (Lazaridis et al., 1991)

$$J_{\text{het}} = \beta Z N_{\text{ads}} \exp \left(\frac{-\Delta G_{\text{het}}^*}{k_b T} \right), \quad (12)$$

where β is the growth rate of the nucleus (Pruppacher & Klett, 2010)

$$\beta = \frac{p}{\sqrt{2\pi k_b T m}}. \quad (13)$$

Here p is the partial pressure of vapour and m is the vapour molecule mass. We approximated Zeldovich correction factor Z with the

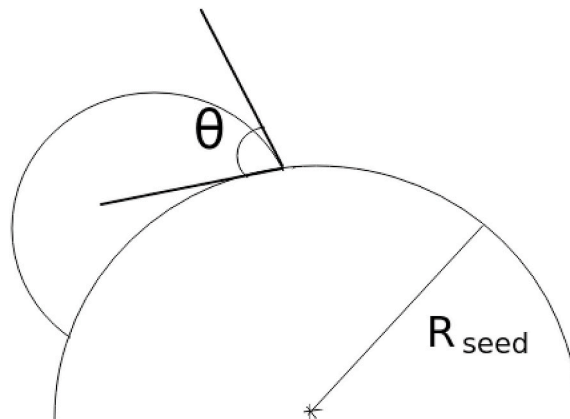


Fig. 1. Schematic illustration of the contact angle in heterogeneous nucleation upon a spherical seed particle with a radius R_{seed} .

value for homogeneous nucleation (Lazaridis et al., 1991):

$$Z = \frac{V}{2\pi r^2} \sqrt{\frac{\sigma_{g,l}}{k_b T}}, \quad (14)$$

where V is the vapour molecule volume. The concentration of vapour molecules on surface of a forming droplet is (Noppel et al., 2007)

$$N_{ads} = \frac{Sp_s}{\sqrt{2\pi mk_b T}} \frac{1}{v} \exp\left(\frac{L}{k_b T}\right), \quad (15)$$

where S is the saturation ratio, p_s is the saturation vapour pressure, v is the vibration frequency of a vapour molecule and L is the latent heat of vapourization per molecule.

Finally, we can calculate the probability of heterogeneous nucleation occurring during a given time span t as (Lazaridis et al., 1992)

$$P_{het} = 1 - \exp(-J_{het} 4\pi R_{seed}^2 t). \quad (16)$$

In this study, we consider the onset of heterogeneous nucleation to correspond to the nucleation probability of 0.5. We defined θ_{max} as the maximum contact angle for which heterogeneous nucleation probability is above 0.5. Thus, when the contact angle is equal to or larger than θ_{max} , heterogeneous nucleation can be considered ineffective. We investigated multiple cases of heterogeneous nucleation by varying the system properties (Table 1). The variables kept constant in the calculations are presented in Table 2. The latent heat of vapourization and vibration frequency of vapour molecule were assumed to be similar enough for different compounds and same values were used for them in all simulations. This was tested by calculating the contact angle corresponding to onset of heterogeneous nucleation for five times larger vibration frequency v , which produced less than a percent of difference in nucleation probability, and for a latent heat 10^{-20} J/molecule larger, which resulted in about three percent difference in nucleation probability.

We have chosen for time parameter t the value of 100 ms, which we have estimated to be longer than the time it takes for a layer of condensed molecules to form on an aerosol particle. Values of t ranging from 1 ms to 1000 s have been used in previous studies of heterogeneous nucleation of atmospheric vapours (Kulmala et al., 2001a; Lazaridis et al., 1992; Winkler et al., 2008b). Because the dependency of θ_{max} on t is relatively weak compared to other factors such as saturation ratio S , molar mass m and surface tension σ , we do not vary t . However, if smaller t was used instead, θ_{max} would also be smaller.

The studied cases included heterogeneous nucleation of a vapour with properties similar to sulphuric acid but with varying vapour concentration, saturation concentration, molecular mass and surface tension. We also studied heterogeneous nucleation of a vapour consisting of clusters of a model low-volatile organic compound (LVOC) molecule or clusters of sulphuric acid (SA) and dimethylamine (DMA). The vapour properties used in calculations are shown in Table 3.

The density of clusters of DMA and SA was calculated according to

$$\rho = \sum_j \frac{N_j \times \rho_j}{N_{tot}}, \quad (17)$$

where N_i is the number of molecules and ρ_i is the density of species i . N_{tot} is the total number of molecules in the cluster. Surface tension was calculated according to

$$\sigma = \sum_j \frac{N_j \times \sigma_j}{N_{tot}}, \quad (18)$$

where σ_j is surface tension of species i .

We also considered the effect of hydration on the surface tension of SA-DMA clusters. According to Henschel et al. (2014) the

Table 1

Different cases for which heterogeneous nucleation probabilities (HNP) were calculated. Here c is vapour concentration, c_{sat} is saturation concentration, σ is surface tension, ρ is density and m is vapour molecule mass. SA stands for sulphuric acid, DMA for dimethylamine and LVOC for low-volatile organic compound.

Investigated issue	c (cm ⁻³)	c_{sat} (cm ⁻³)	σ (N/m)	m (u)	ρ (kg m ⁻³)
1 Dependency of HNP on SA vapour concentration and saturation concentration	$1 \times 10^6 - 2 \times 10^7$	$5 \times 10^4 - 5 \times 10^5$	0.055	98	1830
2 Dependency of HNP on surface tension	1×10^7	1×10^5 & 5×10^5	0.02–0.08	98	1830
3 Dependency of HNP on molecule mass and size	1×10^7	5×10^5	0.055	60–600	1830
4 HNP of SADMA clusters	1×10^7 & 2×10^7	1×10^5	Calculated using Eq. 18	(Number of SA molecules) \times 98 + (Number of DMA molecules) \times 45	Calculated using Eq. 17
5 HNP of LVOC clusters	$5 \times 10^7 - 2 \times 10^8$	3×10^6	0.02	(Number of LVOC molecules) \times 203	1500

Table 2

The variables kept constant when calculating heterogeneous nucleation probabilities. The values for latent heat and vibration frequency are rounded from the values used in Winkler et al. (2008b).

Quantity	Symbol	Value
Time span	t	100 ms
Temperature	T	278.15 K
Latent heat	L	8.0×10^{-20} J/molecule
Vibration frequency	ν	1×10^{12} 1/s

Table 3

Properties of compounds used to calculate heterogeneous nucleation probabilities. SA stands for sulphuric acid, DMA for dimethylamine and LVOC for a low-volatile organic compound.

Compound	Quantity	Value	Reference
sulphuric Acid	m_{SA}	98 u	Haynes (2014)
	σ_{SA}	0.055 N/m	
	ρ_{SA}	1830 kg m^{-3}	
Dimethylamine	m_{DMA}	45 u	Haynes (2014)
	σ_{DMA}	0.026 N/m	
	ρ_{DMA}	650 kg m^{-3}	
LVOC	V_{LVOC}	$135.5 \text{ cm}^3 \text{ mol}^{-1}$	Kulmala et al. (2004)
	σ_{LVOC}	0.02 N/m	
	ρ_{LVOC}	1500 kg m^{-3}	(Ehn et al., 2014)

average number of water molecules is 0.87, 0.41 and 0.20 for clusters of one, two and three SA and one DMA molecule when RH = 30%. Based on this, we chose to investigate cases with vapours consisting of clusters of SA and DMA with an addition of a single water molecule. The density of these clusters was calculated according to Eq. (17) and surface tensions were calculated according to (Hyvärinen et al., 2004). For a water molecule mass we used 18 u and for the density 1000 kg m^{-3} (Haynes, 2014).

2.3. Effective condensation sink and survival probability based on ineffectiveness of heterogeneous nucleation

We studied how ineffectiveness of heterogeneous nucleation affects CS, by assuming that scavenging of vapour molecules or clusters by pre-existing particles occurs only if heterogeneous nucleation of vapour on pre-existing particles is efficient. We assumed that a particle does not act as a sink for vapour molecules or clusters, unless the particle is large enough that heterogeneous nucleation of the vapour onto this particle is effective. First, we calculated CS from Eq. (2) using a measured particle size distribution. Then, we determined CS_{eff} as a function of contact angle of heterogeneous nucleation, by assuming that vapour molecules or clusters are only scavenged by particles for which heterogeneous nucleation is efficient. In addition, to demonstrate the effect of ineffective heterogeneous nucleation on the survival of growing clusters, we determined survival probabilities from 1.5 nm to 3 nm using Eq. (1) by replacing CS with CS_{eff} . We also investigated the effect of contact angle of nucleation on survival probability $J_3/J_{1.5}$.

To calculate CS, we used particle number size distribution data measured at the station of Beijing University of Chemical Technology (39°56'31"N, 116°17'50"E, Beijing) between Jan 17 and March 31 in 2018. The particle size distribution between 1 and 10000 nm was measured with a Diethylene Glycol Scanning Mobility Particle Sizer (Cai et al., 2017a; Jiang et al., 2011) and a custom-made Particle Size Distribution system (Liu et al., 2016). The relative humidity (RH) of the aerosol sample was conditioned to be below 40% by using a Nafion dryer. Therefore, we likely underestimate CS when ambient RH is high, as we do not consider hygroscopic growth of the aerosol population. Previously, hygroscopic growth factor of accumulation mode particles has been estimated to be 1.3 at RH = 90% in winter-time Beijing (Meier et al., 2009). During our measurement period the average ambient RH was 31%, suggesting that hygroscopic growth of the aerosol population was insignificant most of the time.

We calculated CS from the median size distributions determined for NPF event days and haze days between 9:00 and 11:00. A day was classified as an NPF event day if a new mode below 25 nm appeared and the growth of the mode during the following hours was observed. A day was classified as a haze day if visibility was less than 10 km and ambient relative humidity was less than 80%. For more details on this classification and particle size distribution measurements performed at the measurement station, see Zhou et al. (2020).

3. Results

3.1. Effect of system properties on heterogeneous nucleation

Fig. 2 shows θ_{max} for different seed particle diameters in different cases: with sulphuric acid vapour (SA) concentration of $c = 1 \times 10^7 \text{ cm}^{-3}$ and saturation concentration $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3} - 1 \times 10^6 \text{ cm}^{-3}$, and with $c_{\text{sat}} = 5 \times 10^5 \text{ cm}^{-3}$ and $c = 5 \times 10^6 \text{ cm}^{-3} - 2 \times 10^7 \text{ cm}^{-3}$. The corresponding ranges of saturation ratio S are from 100 to 10 and from 10 to 40. The heterogeneous nucleation

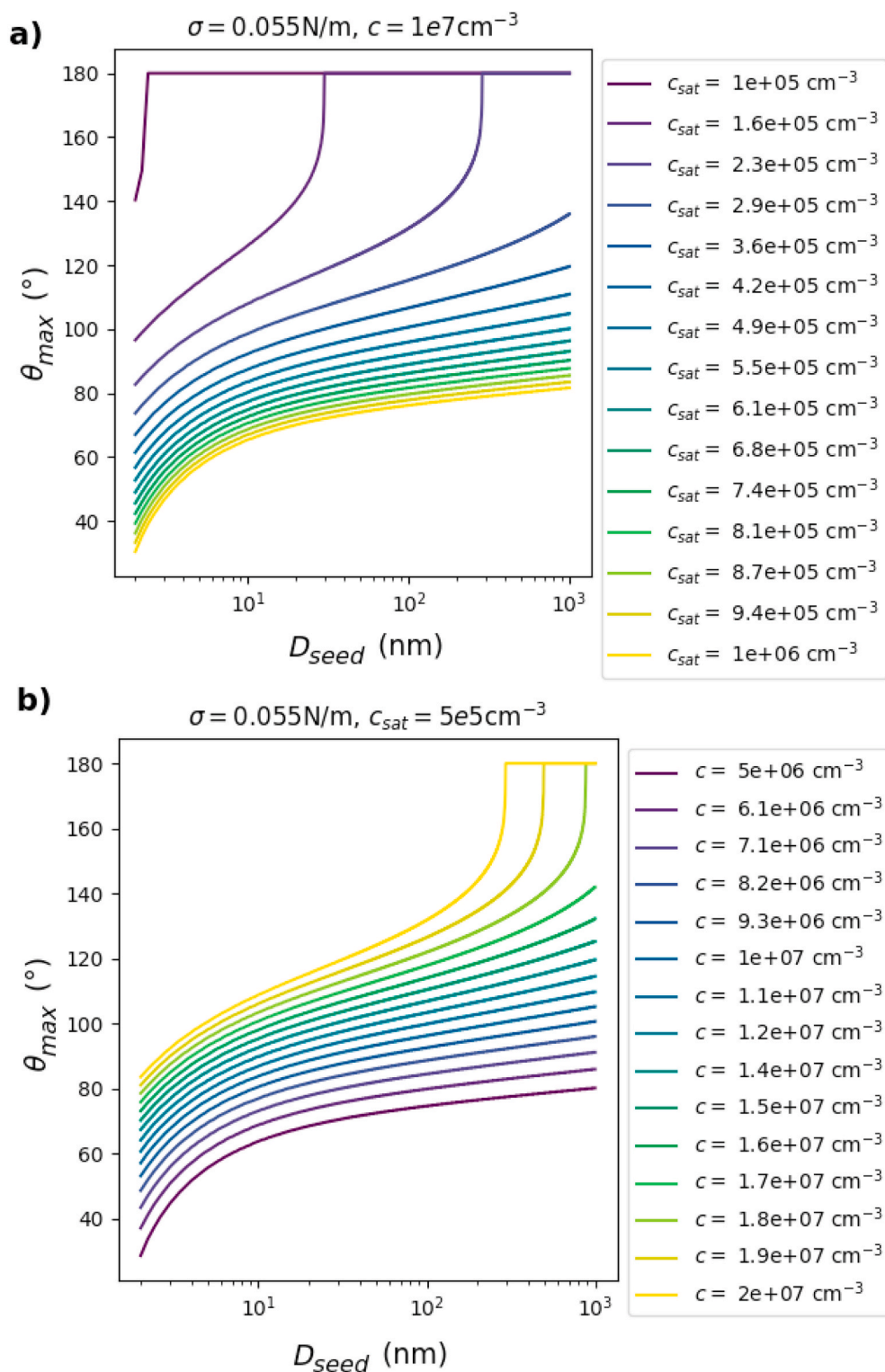


Fig. 2. Maximum contact angle for heterogeneous nucleation to occur (θ_{max}) as a function of seed particle diameter (D_{seed}) (a) for different saturation vapour concentrations $c_{sat} = 1 \times 10^5 \text{ cm}^{-3} - 1 \times 10^6 \text{ cm}^{-3}$ when sulphuric acid concentration is $c = 1 \times 10^7 \text{ cm}^{-3}$, and (b) for $c = 5 \times 10^6 \text{ cm}^{-3} - 2 \times 10^7 \text{ cm}^{-3}$ when c_{sat} is $5 \times 10^5 \text{ cm}^{-3}$.

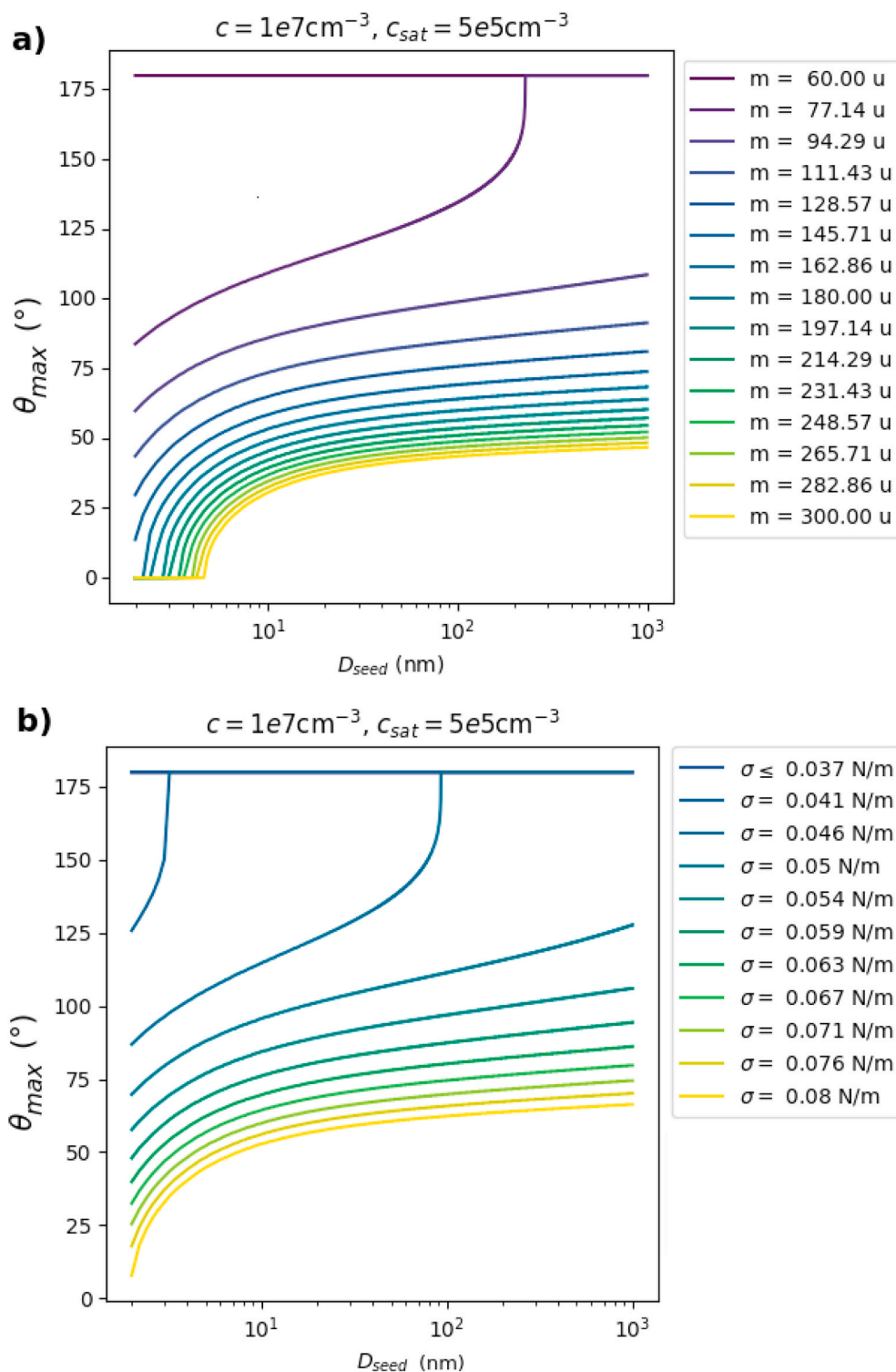


Fig. 3. Maximum contact angle for heterogeneous nucleation to occur (θ_{max}) as a function of seed particle diameter (D_{seed}) for a vapour with properties of sulphuric acid but with (a) mass $m = 60 \text{ u} - 300 \text{ u}$ and (b) with surface tension $\sigma = 0.02 \text{ N/m} - 0.08 \text{ N/m}$. Vapour concentration c is $1 \times 10^7 \text{ cm}^{-3}$ and saturation concentration $c_{sat} = 5 \times 10^5 \text{ cm}^{-3}$.

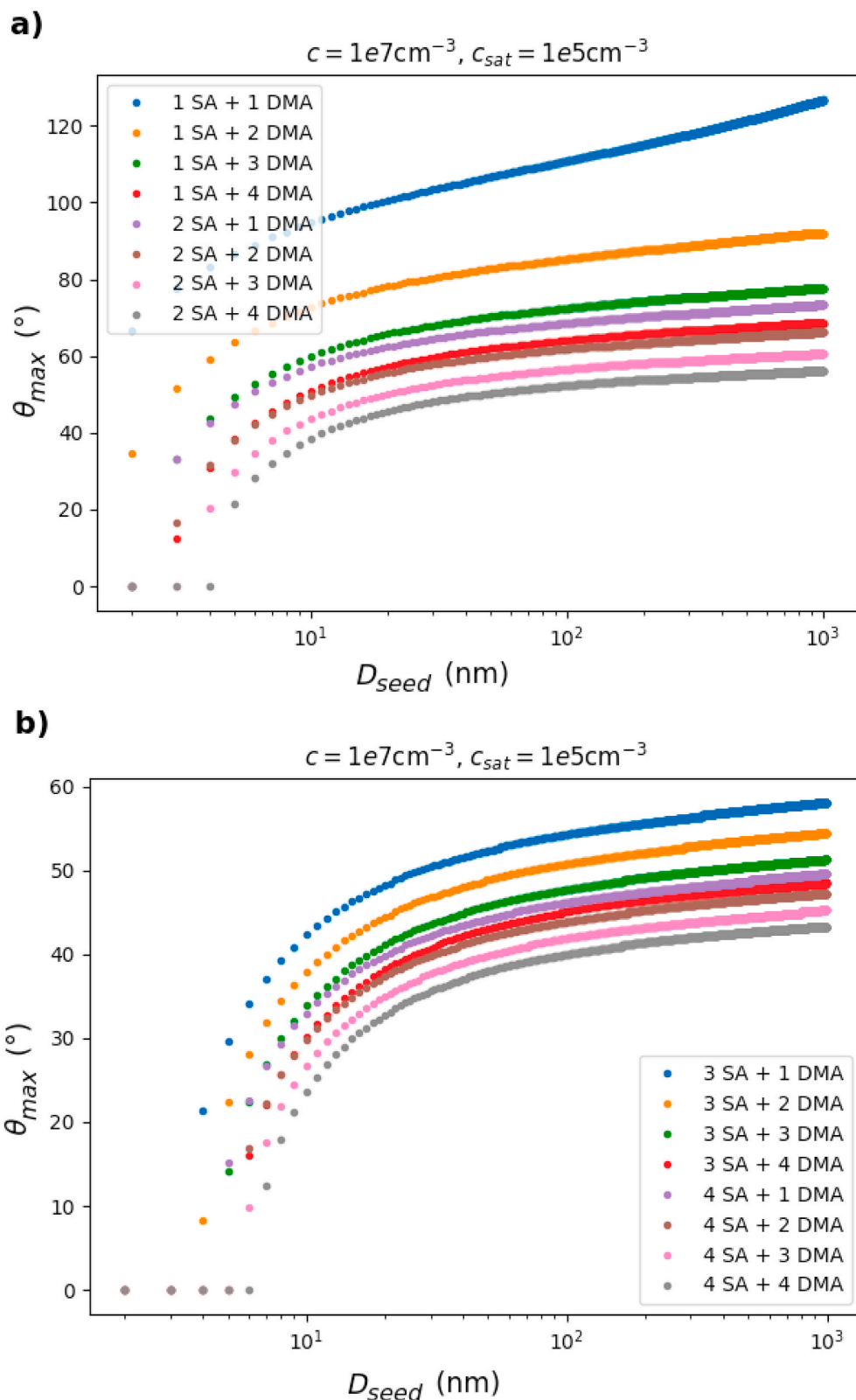


Fig. 4. Maximum contact angle for heterogeneous nucleation to occur (θ_{max}) as a function of seed particle diameter for clusters of sulphuric acid (SA) and DMA when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$, (a) for clusters of one and two SA molecules and one to four DMA molecules, and (b) for clusters of three and four SA molecules and one to four DMA molecules.

probability increases with the decreasing contact angle and the increasing seed particle size. Thus, θ_{max} , needed for heterogeneous nucleation to be ineffective, is larger for larger seed particles. At higher S , heterogeneous nucleation is more favorable and therefore θ_{max} is larger for higher c and lower c_{sat} . These results are in line with previous studies on heterogeneous nucleation probability and nucleation rate (Lazaridis et al., 1991, 1992; Winkler et al., 2008a, b).

In addition to vapour concentration and saturation concentration, θ_{max} also depends on the molecular mass of the compound. Fig. 3a presents θ_{max} as a function of the seed particle diameter for a vapour that has otherwise the properties of SA but different molecular mass at $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{sat} = 1 \times 10^5 \text{ cm}^{-3}$. We can see that when the vapour molecules have larger mass and thus also larger volume, heterogeneous nucleation is less likely and θ_{max} is smaller. At $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{sat} = 5 \times 10^5 \text{ cm}^{-3}$, for a vapour with the molecular mass of 300 u, a contact angle of above 50° is enough for heterogeneous nucleation to be ineffective when the seed particle is smaller or equal to $1 \mu\text{m}$.

Heterogeneous nucleation also depends strongly on the surface tension of the droplet (Fig. 3b). With the higher surface tension, heterogeneous nucleation is less likely and θ_{max} is smaller. If $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{sat} = 5 \times 10^5 \text{ cm}^{-3}$ for the seed diameter of 100 nm and the surface tension of 0.05 N/m, the contact angle has to be over 110° for there to be no heterogeneous nucleation.

Overall, heterogeneous nucleation probability is low, when the contact angle and vapour molecule mass are large and the surface tension of the liquid-gas interface is relatively high. Organic compounds typically have rather low surface tensions (Korosi & Kovats, 1981), which suggests that for them it is less likely to find situations with low heterogeneous nucleation probability than for compounds with higher surface tension. However, organic molecules can also be rather large, which needs to be considered, because the mass of a vapour molecule also strongly affects nucleation probability.

3.2. Heterogeneous nucleation of SA-DMA and LVOC clusters

To study the effectiveness of heterogeneous nucleation for atmospherically relevant compounds, we determined θ_{max} for molecular clusters of sulphuric acid (SA) and dimethylamine (DMA) as well as for molecular clusters of low-volatile organic compound (LVOC).

Fig. 4 presents θ_{max} as a function of seed particle diameter for clusters of SA and DMA. The number of SA and DMA molecules in the clusters varied from one to four molecules and the vapour was assumed to consist of only one type of clusters. DMA has lower surface tension than SA. However, a cluster of only N SA molecules has a higher heterogeneous nucleation probability, and thus higher θ_{max} , than a cluster with N SA molecules with additional DMA molecules, because the latter one has a larger molecular mass. Thus, in this case the effect of larger mass on nucleation probability dominates over the effect of lower surface tension.

From Fig. 4a we can see that for a cluster with one SA molecule and one DMA molecule, heterogeneous nucleation is ineffective when the contact angle is larger than 110° for the seed particle diameter of 100 nm when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{sat} = 1 \times 10^5 \text{ cm}^{-3}$.

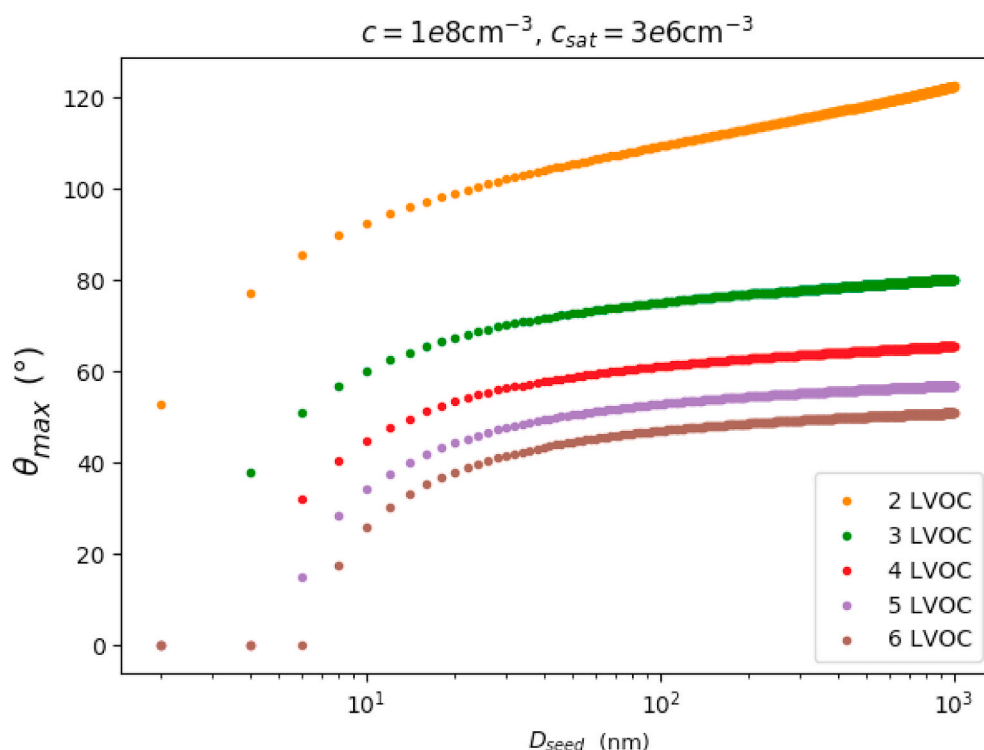


Fig. 5. Maximum contact angle for heterogeneous nucleation to occur (θ_{max}) as a function of seed particle diameter (D_{seed}) for clusters of exemplary LVOC molecules when $c = 1 \times 10^8 \text{ cm}^{-3}$ and $c_{sat} = 3 \times 10^6 \text{ cm}^{-3}$.

Thus, with this contact angle, clusters composed of SA and DMA would not be scavenged by particles smaller than 100 nm. If the cluster is composed of two SA and two DMA molecules, a smaller contact angle of 60° is sufficient for heterogeneous nucleation to be ineffective.

One should note that in atmospheric conditions, clusters composed of SA and DMA likely also contain water. We consider the effects of hydration more in subsection 3.4.

We investigated heterogeneous nucleation of low-volatile organic compound for different sized clusters consisting of an exemplary LVOC molecule at $c = 1 \times 10^8 \text{ cm}^{-3}$ and $c_{\text{sat}} = 3 \times 10^6 \text{ cm}^{-3}$. θ_{max} for LVOC clusters are shown in Fig. 5. For a vapour of single LVOC molecules, heterogeneous nucleation occurs with all the contact angles due to the low surface tension of LVOC. For a cluster of two LVOC molecules, a contact angle needs to be slightly higher than 100° for no heterogeneous nucleation to occur if the seed particle diameter is 100 nm. For a massive cluster of six LVOC molecules θ_{max} is only around 40° , even if the seed particle has a diameter close to $1 \mu\text{m}$. This means that very large organic molecules are unlikely to condense on aerosol particles if the contact angle is not smaller than 40° .

3.3. Effect of ineffective heterogeneous nucleation on condensation sink

We used a median size distribution measured in Beijing during NPF (Fig. 6) to calculate CS according to Eq. (2). Then, by using the same size distribution, the values of CS_{eff} were calculated assuming that particles below certain diameters do not contribute to CS, i.e. for them factor ζ_i in Eq. (5) is zero. The size below which particles were assumed not to contribute to CS was determined as the size where heterogeneous nucleation becomes ineffective for the studied compound and contact angle.

In addition, we performed some of the calculations using a median size distribution at 9:00–11:00 on haze days (Fig. 6). These are discussed in the end of the section. During haze days, number concentrations of particles smaller than 10 nm were lower than during NPF, while concentration of larger particles were clearly higher with the maximum concentration observed for particles with diameters of around 200 nm.

Fig. 7 shows the ratio between CS_{eff} and CS for the size distribution during NPF as a function of the contact angle for SA concentration $c = 5 \times 10^6 \text{ cm}^{-3} - 2 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3} - 1 \times 10^6 \text{ cm}^{-3}$. The corresponding ranges of saturation ratio S are from 100 to 10 and from 10 to 40. For all these cases, the contact angle has to be over 70° to significantly reduce CS_{eff} compared to CS. For a contact angle of 75° and $c = 5 \times 10^6 \text{ cm}^{-3}$, CS_{eff} is about 20% of the actual CS for SA when $c_{\text{sat}} = 5 \times 10^5 \text{ cm}^{-3}$ (Fig. 7b). Assuming $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$ and $c = 1 \times 10^7 \text{ cm}^{-3}$ (Fig. 7a), CS_{eff} is equal to CS for all θ .

Fig. 8a shows $\text{CS}_{\text{eff}}/\text{CS}$ as a function of contact angle for $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 5 \times 10^5 \text{ cm}^{-3}$. The vapour has otherwise the properties of SA but the molecular mass m is varied between 60 u and 300 u. Assuming $m = 300$ u, the contact angle has to be only around 40° for CS_{eff} to be 50% of CS. However, if $m = 200$ u, the contact angle has to be around 60° to have the same effect.

Fig. 8b shows $\text{CS}_{\text{eff}}/\text{CS}$ as a function of the contact angle for vapour concentration of $1\text{e}7 \text{ cm}^{-3}$ and saturation concentration of $5\text{e}5 \text{ cm}^{-3}$. The vapour has otherwise the properties of SA but surface tension is varied from 0.02 N/m to 0.08 N/m. If the surface tension is 0.08 N/m and the contact angle is 70° , the ratio between CS_{eff} and CS is very small. However, with the surface tension of 0.041 N/m and lower, CS_{eff} and CS are equal, unless the seed and vapour completely repel each other.

We also studied the effect of inefficient heterogeneous nucleation on CS_{eff} for molecular clusters of SA and DMA (Fig. 9). For a cluster with one SA and one DMA molecule (Fig. 9a), the contact angle has to be over 100° to have a notable effect on CS_{eff} and over 110° for CS_{eff} to be half, or less, of CS. Assuming that the molecular clusters have three SA molecules and one DMA molecule (Fig. 9b), the contact angle of about 60° results in CS_{eff} that is close to zero. Thus, for a real nucleating vapour, consisting of different sized clusters, all clusters with at least three SA molecules and one DMA molecule would not effectively take part in heterogeneous

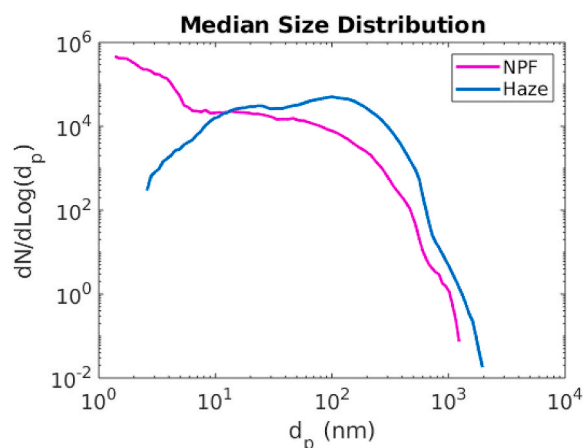


Fig. 6. Median particle number size distribution between 9:00 and 11:00 in Beijing, China, on new particle formation event (NPF) days (magenta line) and on haze days (blue line). For details on particle size distribution measurements performed at the measurement station, see Zhou et al. (2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

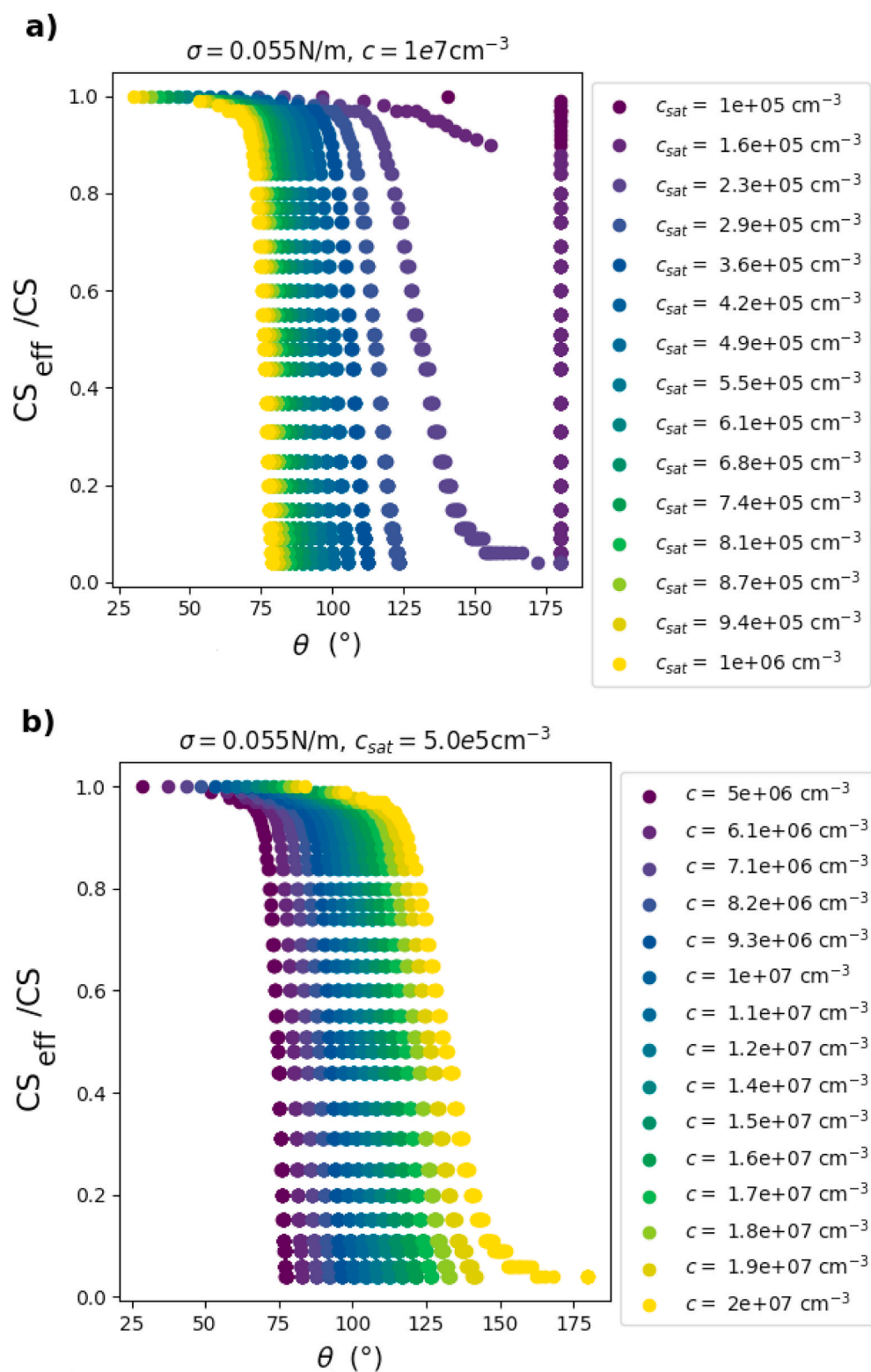


Fig. 7. Ratio of effective condensation sink (CS_{eff}) and condensation sink (CS) as a function of contact angle θ (a) for different saturation vapour concentrations $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3} - 1 \times 10^6 \text{ cm}^{-3}$ when sulphuric acid vapour concentration is $c = 1 \times 10^7 \text{ cm}^{-3}$, and (b) for $c = 5 \times 10^6 \text{ cm}^{-3} - 2 \times 10^7 \text{ cm}^{-3}$ when $c_{\text{sat}} = 5 \times 10^5 \text{ cm}^{-3}$.

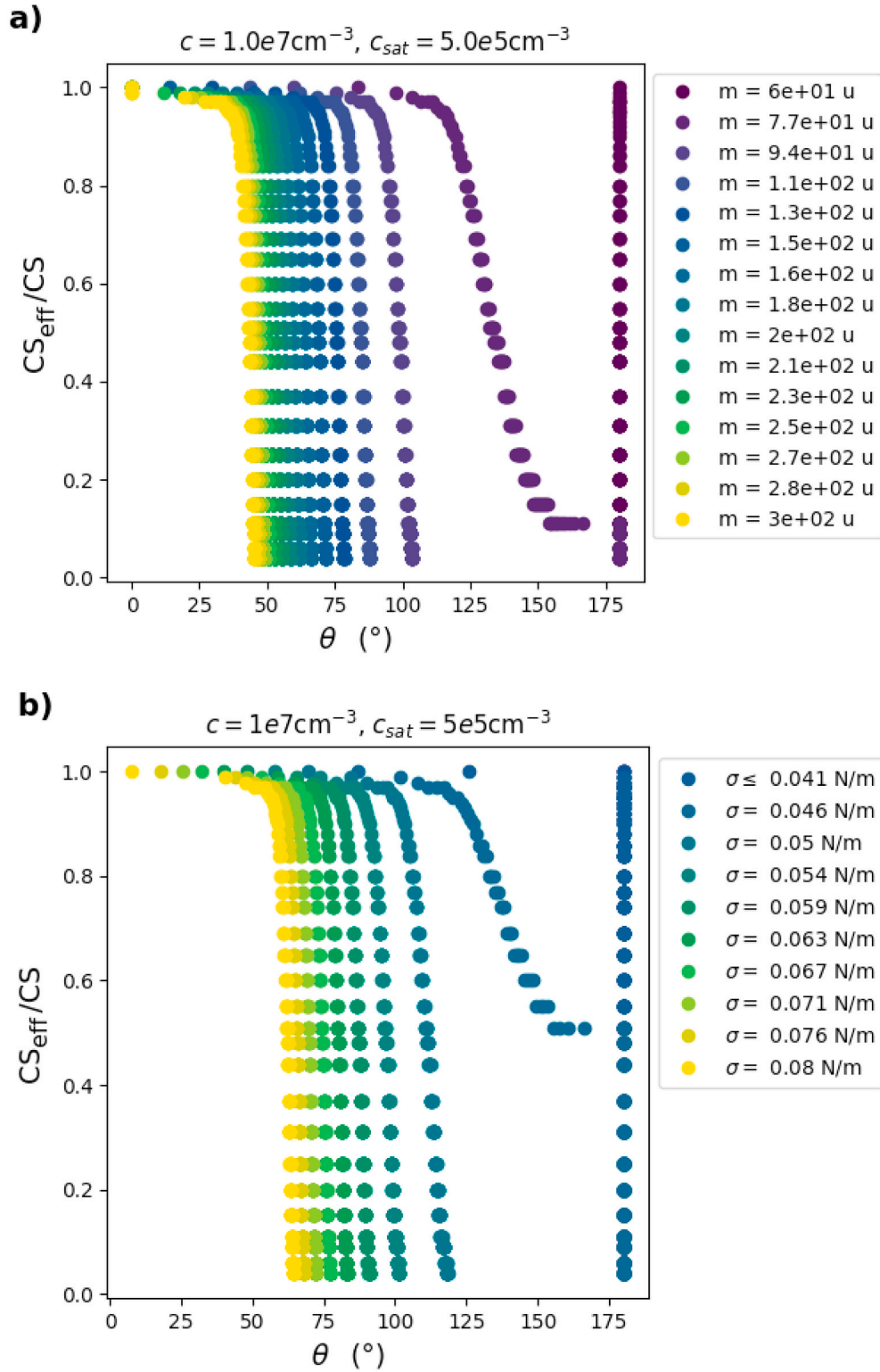


Fig. 8. Ratio between effective condensation sink (CS_{eff}) and condensation sink (CS) as a function of contact angle θ for a vapour with properties of sulphuric acid but (a) with mass $m = 60$ u – 300 u and (b) with surface tension $\sigma = 0.02$ N/m – 0.08 N/m. Vapour concentration is $c = 1 \times 10^7 \text{ cm}^{-3}$ and saturation concentration $c_{\text{sat}} = 5 \times 10^5 \text{ cm}^{-3}$.

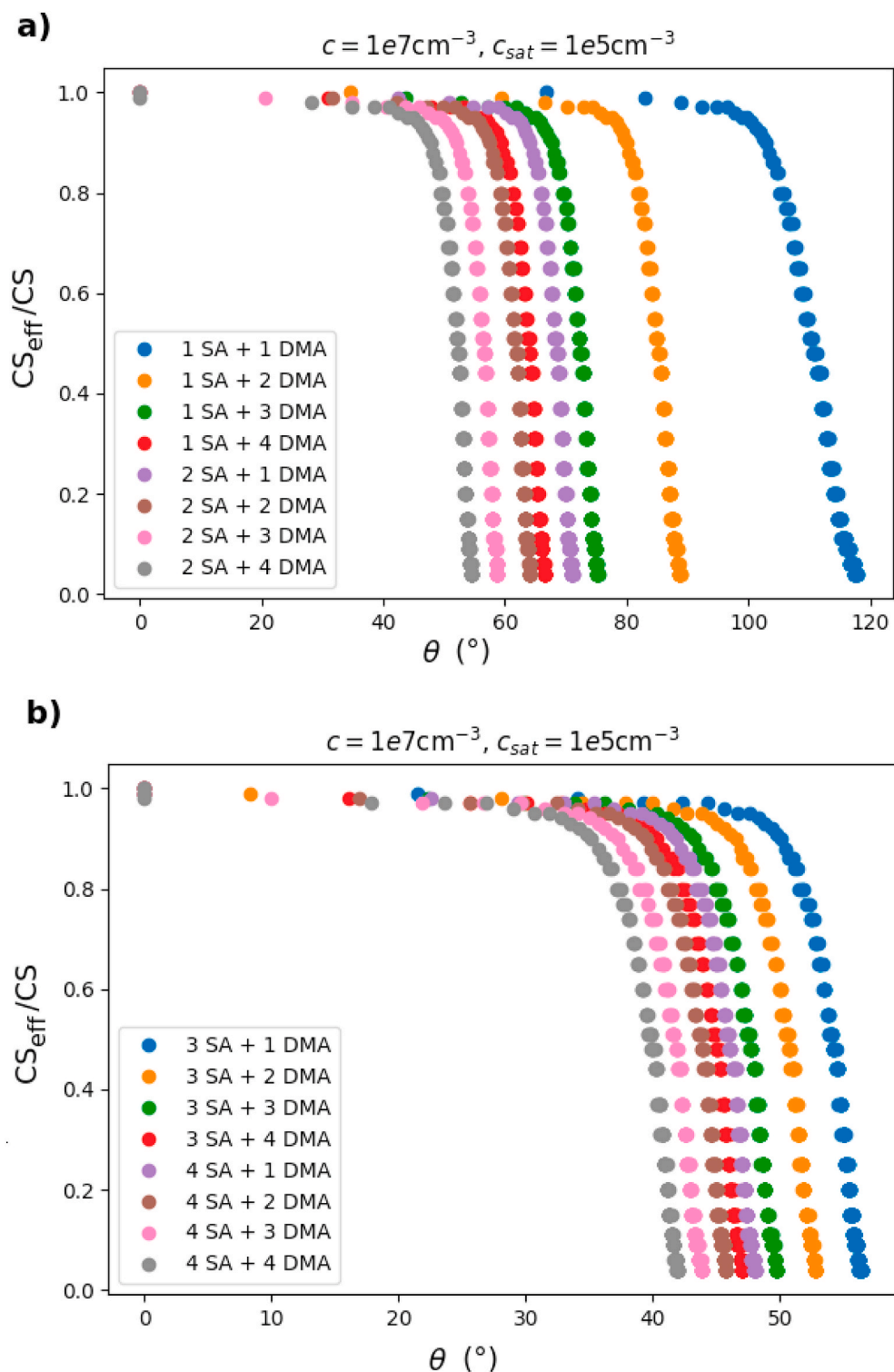


Fig. 9. Ratio between effective condensation sink (CS_{eff}) and condensation sink (CS) as a function of contact angle θ for clusters of sulphuric acid (SA) and DMA when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$, (a) for clusters of one and two SA molecules and one to four DMA molecules, and (b) for clusters of three and four SA molecules and one to four DMA molecules.

nucleation if the average contact angle was about 60° . In other words, these clusters would not be scavenged by the seed particles.

Fig. 10 presents CS_{eff}/CS for different contact angles for clusters of LVOC molecules. If the clusters consist of two LVOC molecules, the contact angle has to be over 110° to have a significant effect on CS_{eff} . However, if the clusters have six LVOC molecules, a contact angle of above 45° is enough for CS_{eff} to be half of the CS. For a cluster with just a single LVOC molecule, heterogeneous nucleation is effective at all contact angles.

Finally, we compared CS_{eff}/CS calculated from the size distribution during NPF events to CS_{eff}/CS determined from the size distribution during haze (see Fig. 6). As we can see from Fig. 11, the behaviour and values of CS_{eff}/CS are similar during both NPF events and haze events. For a size distribution during haze, CS_{eff}/CS declines more strongly with the increasing contact angle, but also starts to drop at larger contact angles compared to NPF. The differences become more significant with decreasing cluster mass. For a cluster of one SA molecule and one DMA molecule at $\theta = 110^\circ$, CS_{eff}/CS is about 0.5 for NPF events while for haze events CS_{eff}/CS is over 0.9 (Fig. 11a). For a cluster of two LVOC molecules at $\theta = 110^\circ$, CS_{eff}/CS is around 0.4 for NPF events while for haze events CS_{eff}/CS is over 0.9. For a cluster of six LVOC molecules at $\theta = 40^\circ$, CS_{eff}/CS is around 0.9 for NPF events while for haze events CS_{eff}/CS equals one (Fig. 11b).

3.4. Effect of hydration of clusters on effective condensation sink

In atmospheric conditions, the clusters of SA and DMA likely also contain some water (Henschel et al., 2014). We investigated the effect of hydration of clusters on CS_{eff} by assuming that SA-DMA clusters also include one water molecule. Fig. 12 shows CS_{eff}/CS during NPF as a function of θ for vapours consisting of SA, DMA and water, and for a comparison, for vapours consisting of only SA and DMA. We can see that addition of water lowers CS_{eff} for all the clusters, due to the increased mass and surface tension of the clusters. For the clusters of 1 SA + 1 DMA, CS_{eff}/CS is 0.5 when $\theta = 110^\circ$, while for the clusters of 1 SA + 1 DMA + 1 H₂O similar CS_{eff}/CS results from $\theta = 60^\circ$. For the clusters of 3 SA + 1 DMA, CS_{eff}/CS is 0.5 when $\theta = 55^\circ$ and for the clusters of 3 SA + 1 DMA + 1 H₂O when $\theta = 45^\circ$. The effect of added water is smaller for the clusters with more SA and DMA due to the smaller mole fraction of water.

3.5. Effective condensation sink and survival probability

To demonstrate the connection between lower a CS_{eff} and a higher survival probability of growing clusters, we calculated the probabilities that 1.5 nm clusters survive to 3 nm particles, $J_3/J_{1.5}$, corresponding to CS_{eff} during NPF using Eq. (1). Three different growth rates, GR = 1.5, 3, 6 nm/h, were used. Fig. 13a shows $J_3/J_{1.5}$ for different CS_{eff}/CS and Fig. 13b the corresponding relative increase in $J_3/J_{1.5}$. We can see that when CS_{eff} is equal to CS, $J_3/J_{1.5}$ is low. With GR = 3 nm/h, which corresponds to a typical GR in Beijing (Zhou et al., 2020), $J_3/J_{1.5}$ is around 0.05 at $CS_{\text{eff}}/CS = 1$. This means that practically no particles survive to 3 nm. However,

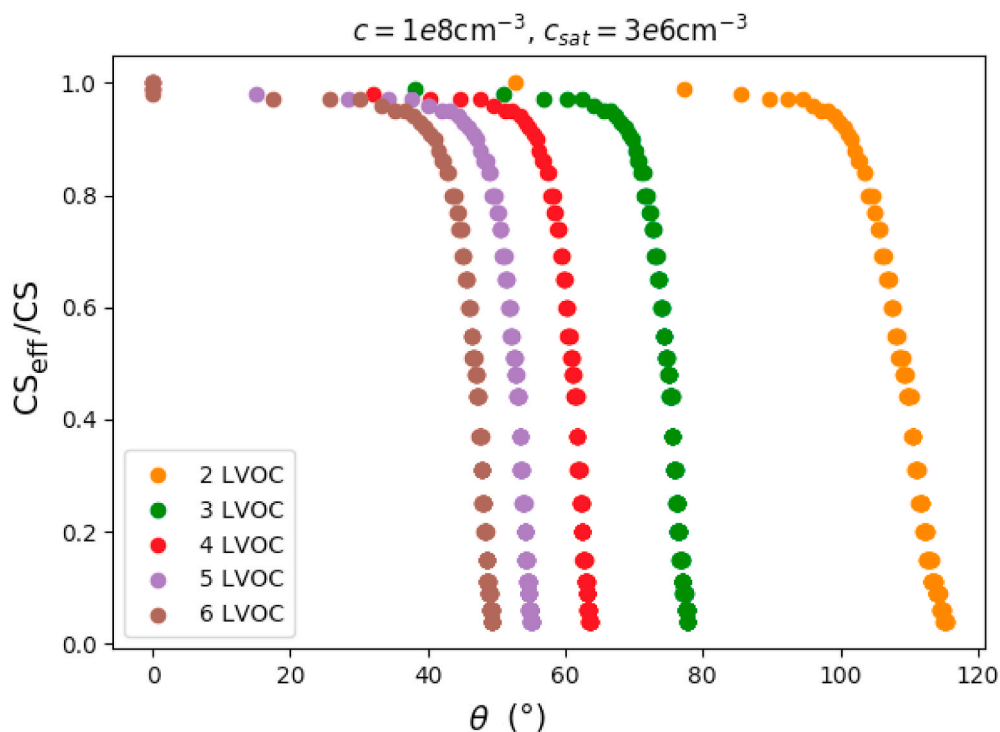


Fig. 10. Ratio between effective condensation sink and condensation sink as a function of contact angle θ for clusters of model LVOC molecule when $c = 1 \times 10^8 \text{ cm}^{-3}$ and $c_{\text{sat}} = 3 \times 10^6 \text{ cm}^{-3}$.

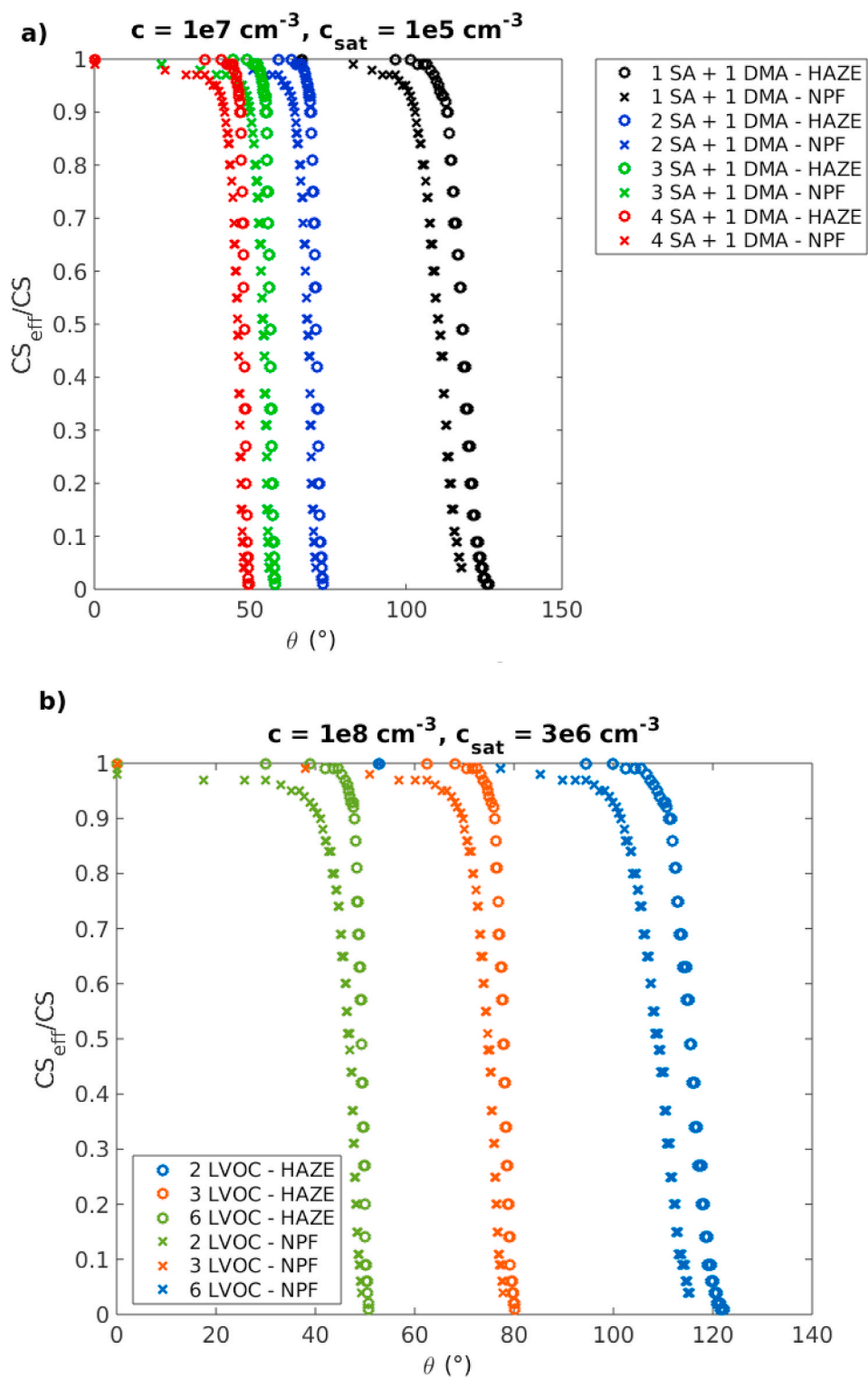


Fig. 11. Ratio between effective condensation sink and condensation sink as a function of contact angle θ , for clusters consisting of (a) one to four sulphuric acid (SA) molecules and one dimethylamine (DMA) molecule during a haze event and NPF event when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$, (b) and of model LVOC molecule when $c = 1 \times 10^8 \text{ cm}^{-3}$ and $c_{\text{sat}} = 3 \times 10^6 \text{ cm}^{-3}$, during a haze event and NPF event.

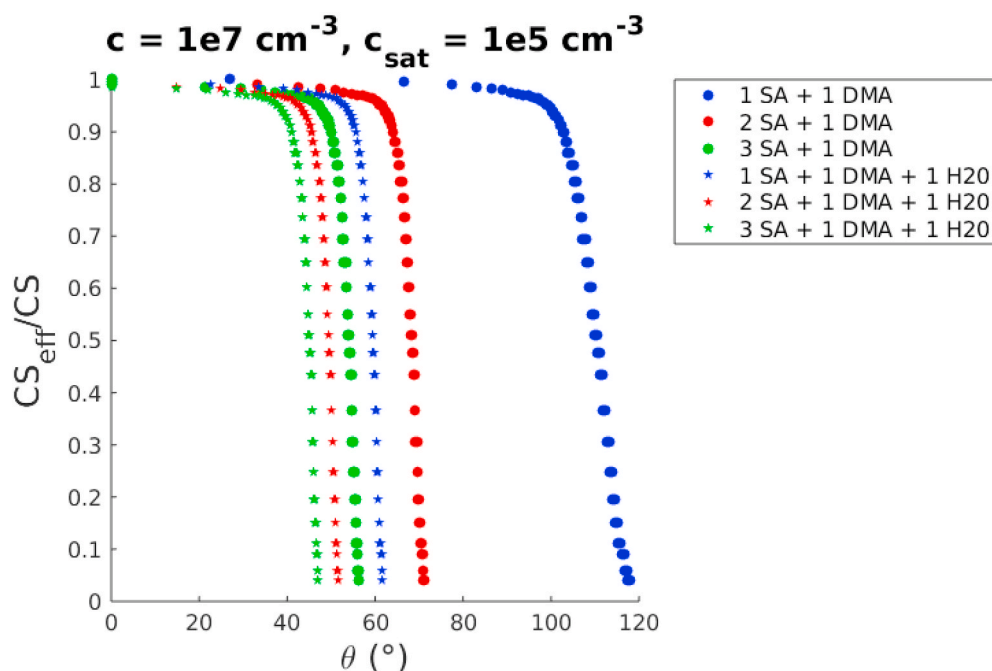


Fig. 12. Ratio of effective condensation sink and condensation sink (CS_{eff}/CS) as a function of contact angle (θ) of heterogeneous nucleation for vapours with clusters of one to three sulphuric acid (SA) molecules, single DMA molecule and a single water molecule when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$. Vapours with no water are included for a comparison.

when CS_{eff}/CS decreases, $J_3/J_{1.5}$ clearly increases. When CS_{eff}/CS is 0.2, $J_3/J_{1.5}$ is already 0.5, which is over 10 times higher than when $CS_{\text{eff}} = CS$.

In Fig. 14a we see θ and $J_3/J_{1.5}$ for vapours of SA and DMA. Assuming a vapour of 1 SA + 1 DMA and $\theta = 115^\circ$, $J_3/J_{1.5} = 0.5$. This means that $J_3/J_{1.5}$ is around 13 times larger than when $\theta = 0^\circ$ (Fig. 14b). When the contact angle of nucleation is larger, heterogeneous nucleation becomes less effective. This results in decreased CS_{eff} , and thus increased survival probability. This result illustrates that the occurrence of NPF events in Chinese megacities can be explained by using our theoretical approach, assuming that the contact angle of nucleation is large enough.

3.6. Atmospheric relevance of the results

Evaluating the atmospheric relevance of our results is difficult, because there exist little data on the relevant properties of compounds participating in atmospheric NPF, such as their saturation ratios (determined by vapour concentration and saturation concentration) and contact angles. Heterogeneous nucleation probability strongly depends on these properties and changes in them can drastically change the magnitude of nucleation probability (Lazaridis et al., 1991, 1992; Winkler et al., 2008, b). Classical Nucleation Theory of heterogeneous nucleation has also been shown to fail in adequately describing experimental nucleation rates (Gorbunov and Kakutkina, 1982; Lauri et al., 2006), which may limit the accuracy of our results.

The contact angle for pure SA on seed particles consisting of sulfur has been estimated to be around 70° (Hamill et al., 1982). If we assume that scavenging of vapour by pre-existing particles in Beijing can be described by heterogeneous nucleation of pure SA on sulfur particles, ineffective heterogeneous nucleation does not reduce CS_{eff} during NPF at $c_{\text{sat}} \leq 1 \times 10^6 \text{ cm}^{-3}$ if $c = 1 \times 10^7 \text{ cm}^{-3}$ (Fig. 7). However, if we assume that the vapour consists of clusters of SA and DMA with the same contact angle as pure SA on sulfur, CS_{eff} can be significantly lowered. For example, with $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{\text{sat}} = 1 \times 10^5 \text{ cm}^{-3}$, CS_{eff}/CS is 0.5, or smaller, during both NPF and haze, if clusters have one DMA molecule and at least two SA molecules (Fig. 11a). CS_{eff}/CS being 0.5, or smaller, results in $J_3/J_{1.5}$ during NPF being at least 6 times higher than if CS_{eff}/CS equals one, assuming $GR = 3 \text{ nm/h}$.

However, the contact angle of nucleation also depends on the properties of the seed particle (Eq. (11)) and in the atmosphere the seed particles can have varying chemical composition. In addition, for compounds with lower surface tension, the contact angle of heterogeneous nucleation on the same surface is lower (Sullivan, 1981). We have also shown that for the same contact angle and surface tension, a lower molecular mass leads to a higher nucleation probability. Thus, it is likely that for compounds with low surface tension and a relatively small molecular mass, the impact of ineffective heterogeneous nucleation on condensation sink is insignificant. As sulphuric acid typically has higher surface tension than organic compounds, the effective condensation sink is likely lower for sulphuric acid than for organic species of similar molecular weight.

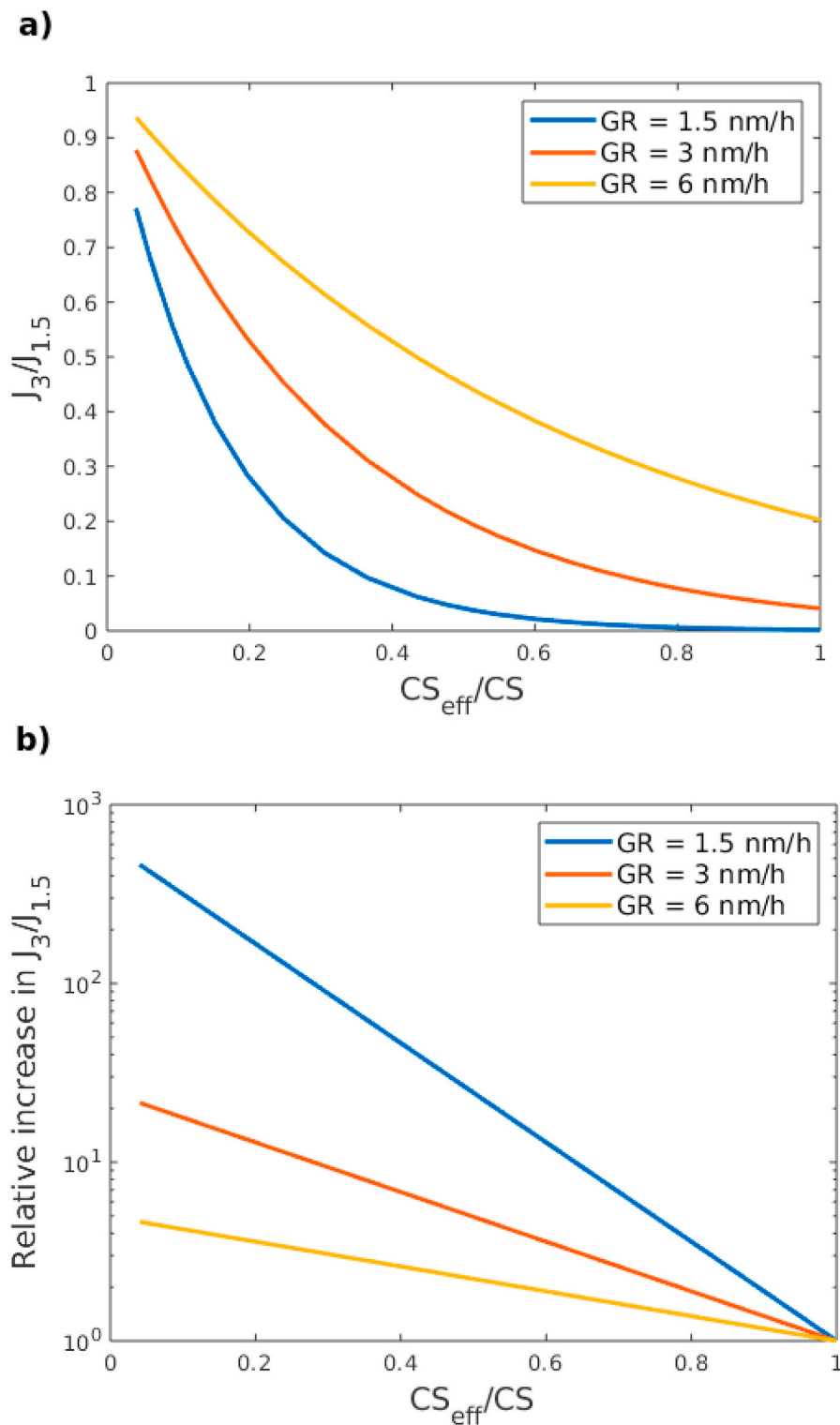


Fig. 13. (a) Survival probability $J_3/J_{1.5}$ as a function of the ratio of effective condensation sink and condensation sink (CS_{eff}/CS) and (b) the relative increase in $J_3/J_{1.5}$, compared to when $CS_{\text{eff}} = CS$, as a function of CS_{eff}/CS . The values are calculated for NPF event times assuming particle growth rate $GR = 1.5 \text{ nm/h}$, 3 nm/h and 6 nm/h .

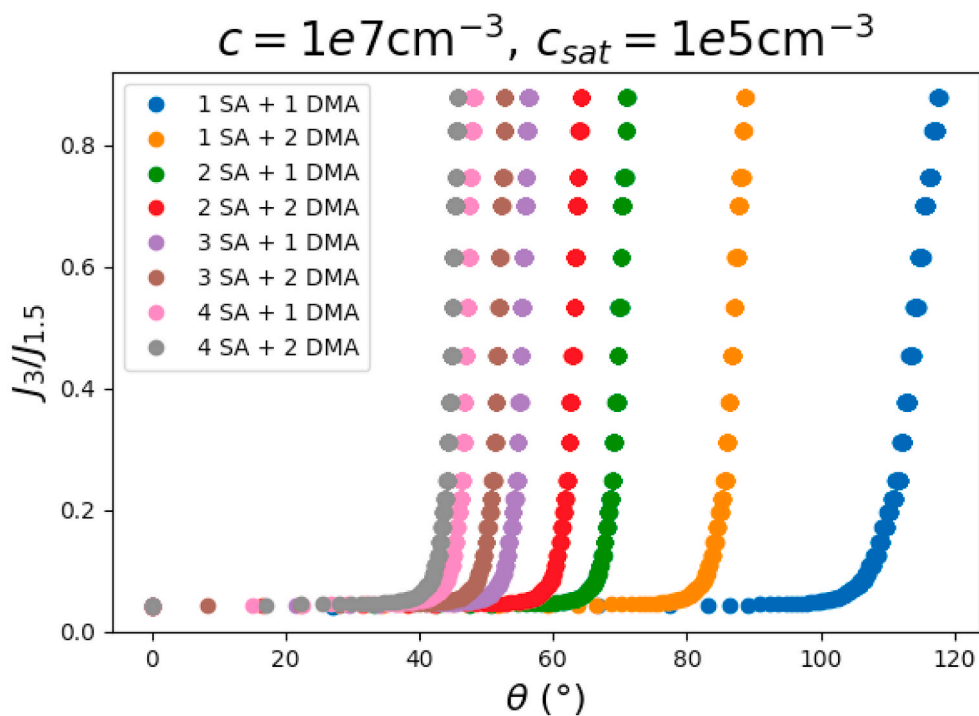
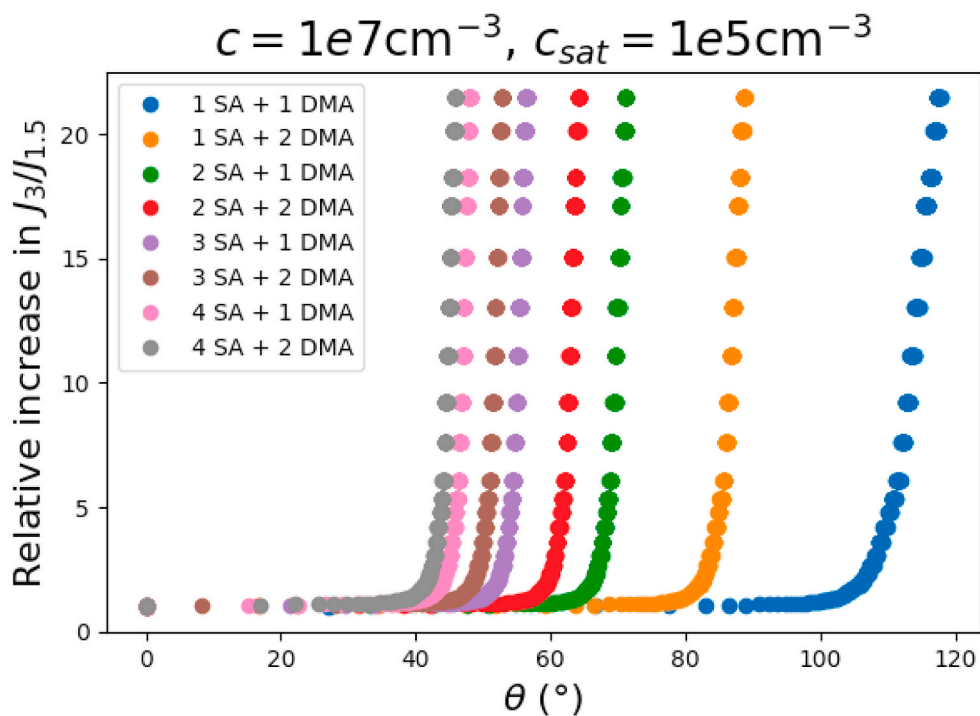
a)**b)**

Fig. 14. (a) Survival probability $J_3/J_{1.5}$ as a function of contact angle θ and (b) relative increase in $J_3/J_{1.5}$, compared to when $\theta = 0^{\circ}$, as a function of θ for clusters of one to four sulphuric acid (SA) molecules and one or two DMA molecules when $c = 1 \times 10^7 \text{ cm}^{-3}$ and $c_{sat} = 1 \times 10^5 \text{ cm}^{-3}$.

4. Conclusions

In theory, NPF events should not happen if condensation sink (CS), caused by pre-existing particle population, is very high, due to the low survival probability of growing clusters. Still, NPF events are regularly observed in heavily polluted environments, such as Chinese megacities. In this study, we explored possible explanations for this discrepancy. We described the loss of vapour molecules and clusters due to CS by using heterogeneous nucleation theory, and investigated if ineffectiveness of heterogeneous nucleation can result in a significantly lowered effective condensation sink (CS_{eff}) in different atmospherically relevant situations.

We found that heterogeneous nucleation probability strongly depends on the saturation ratio of the vapour, determined by the ratio between the concentration and saturation concentration of the vapour. In addition, heterogeneous nucleation probability is strongly affected by the contact angle of nucleation. When the contact angle is large, it is possible to find situations where heterogeneous nucleation is unlikely. Also, for chemical compounds with relatively large molecular mass or high surface tension, heterogeneous nucleation is inefficient.

Overall, we observed that for CS_{eff} to be significantly lower than CS, the vapour needs to have relatively large molecular mass or high surface tension, or the contact angle of nucleation has to be large. For example, for a vapour consisting of sulphuric acid and DMA clusters, CS_{eff} can be clearly lower than CS due to inefficient heterogeneous nucleation, which can result in a significant increase in the survival probability of clusters growing to larger particles. This implies that inefficient heterogeneous nucleation could, in principle, explain unexpected high survival probability of clusters in Chinese megacities, where nucleation of sulphuric acid and DMA has been suggested to drive the first steps of NPF (Yao et al., 2018). However, as the contact angle of nucleation and the exact properties of vapours are unknown, if this really is the case remains unresolved. Therefore, further studies, especially focusing on the contact angle of nucleation of atmospherically relevant compounds, are needed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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